

**PROCESS INTEGRATION ISSUES
OF LOW-PERMITTIVITY DIELECTRICS
WITH COPPER FOR HIGH-PERFORMANCE
INTERCONNECTS**

A DISSERTATION

SUBMITTED TO THE DEPARTMENT OF ELECTRICAL ENGINEERING

AND THE COMMITTEE ON GRADUATE STUDIES

OF STANFORD UNIVERSITY

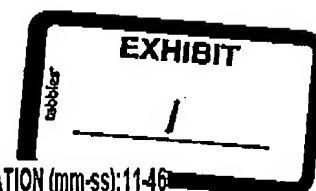
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF Ph.D.

CHAPTER 3

Alvin Leng Sun Loke

March 1999



Chapter 3 Low-Permittivity Dielectrics

Interlevel dielectrics (ILD's) currently incorporated in IC manufacturing are deposited oxides with dielectric constants (κ 's) ranging from 4.0 to 4.5. As explained in Chapter 1, substituting the oxide ILD's with lower κ materials improves the performance of interconnects through reduction of parasitic capacitance. Capacitance reduction mitigates crosstalk noise, dynamic power dissipation, and interconnect propagation delay issues as interconnects continue to scale.

This chapter focusses on the chemistry and materials aspects of low-permittivity (low- κ) dielectrics, starting with a brief discussion of the physical properties that make a dielectric low- κ . A survey of materials that are developed as prospective future ILD materials is then presented. Emphasis is placed on the six low- κ polymer dielectrics that are studied in this dissertation.

3.1 Strategies for Dielectric Constant Reduction

The dielectric constant, κ , is a physical measure of the electric polarizability of a material [68]. Electric polarizability is the tendency of a material to allow an externally applied electric field to induce electric dipoles (separated positive and negative charges) in the material. Shown in Eq. (3-1), κ can be expressed as

Chapter 3: Low-Permittivity Dielectrics

$$\kappa = \frac{\epsilon}{\epsilon_0} = \frac{\epsilon_0(1 + \chi_e)}{\epsilon_0} = 1 + \chi_e \quad (3-1)$$

where ϵ and ϵ_0 are the permittivities of the dielectric and free space respectively, and χ_e is the electric susceptibility of the dielectric. χ_e is the unitless constant of proportionality relating the induced dipole moment per unit volume of dielectric, \vec{P} , to the applied electric field, \vec{E} .

$$\vec{P} = \epsilon_0 \chi_e \vec{E} \quad (3-2)$$

In a perfect vacuum, there are no atoms to polarize, making $\chi_e = 0$ and $\kappa = 1$. In solid-state matter, there are three polarization mechanisms: electronic, atomic, and dipolar [69]. Electronic polarization occurs in neutral atoms when an electric field displaces the nucleus with respect to the electrons that surround it. Atomic polarization occurs when adjacent positive and negative ions stretch under an applied electric field. Dipolar or orientational polarization occurs when permanent dipoles in asymmetric molecules respond to the applied electric field. Each polarization mechanism has an associated response time and therefore will not contribute to κ beyond some corresponding frequency. Figure 3-1 illustrates a typical κ dependence on the frequency of the applied field. All three mechanisms respond to GHz or lower frequencies where IC's operate.

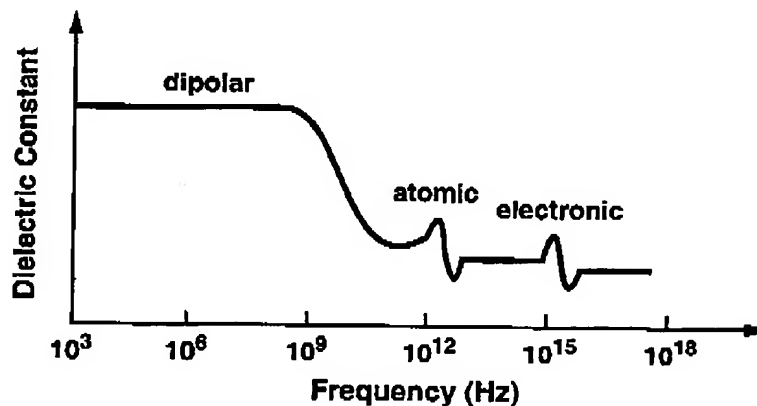


Figure 3-1 Frequency response of dielectric mechanisms [69].

3.2 Survey of Available Materials

A low- κ dielectric is an insulating material that exhibits weak polarization when subjected to an externally applied electric field. There are many guidelines employed to design low- κ materials. A few practical approaches are briefly mentioned. The most obvious one is to choose a nonpolar dielectric system. For example, polarity is weak in materials with few polar chemical groups and with symmetry to cancel the dipoles of chemical bonds between dissimilar atoms. Since $\kappa_{air} \approx 1$, dielectrics can also have lower effective κ 's with the incorporation of some porosity into the chemical structure. Another approach is to minimize the moisture content in the dielectric or alternatively design a dielectric with minimum hydrophilicity. Since $\kappa_{water} \approx 80$, a low- κ dielectric needs to absorb only very small traces of water before losing its permittivity advantage.

3.2 Survey of Available Materials

Strictly speaking, air has the lowest κ , exhibiting more than 75% permittivity improvement over conventional oxide ILD's. Unfortunately, many reliability concerns exist with the implementation of air as the ILD, the obvious one being the structural integrity of the interconnects. Some of these issues can be mitigated by deliberately integrating air voids, for example, using an unconformal oxide deposition during gapfill [70]. However, the manufacturability of these approaches remain to be demonstrated. For a low- κ

Table 3-1: Property Requirements of Low- κ Dielectrics

Electrical	Chemical	Mechanical	Thermal
Dielectric constant	Chemical resistance	Thickness uniformity	High thermal stability
Anisotropy	Etch selectivity	Good adhesion	Low coefficient of thermal expansion
Low dissipation	Low moisture uptake	Low stress	Low thermal shrinkage
Low leakage current	Low solubility in H ₂ O	High hardness	Low thermal weight loss
Low charge trapping	Low gas permeability	Low shrinkage	High thermal conductivity
High electric-field strength	High purity	Crack resistance	
High reliability	No metal corrosion	High tensile modulus	
	Long storage life		
	Environmentally safe		

Chapter 3: Low-Permittivity Dielectrics

dielectric to be considered suitable for backend integration, it must satisfy a multitude of electrical, chemical, mechanical, and thermal requirements summarized in Table 3-1. These requirements invariably introduce compromises which must be carefully considered in order to engineer feasible low- κ materials for the ILD application.

The families of dielectric materials currently available for ILD integration are listed in Table 3-2. These dielectrics are deposited on the wafer either by CVD or by spin-on deposition. CVD offers the advantages of being a dry process, capable of producing films with excellent uniformity and conformality [71]. However, CVD is generally restricted to dielectrics with relatively simple chemistries. A larger variety of materials can be deposited by spin-on deposition [72], much like photoresist. Dissolved in a solvent, spin-on low- κ precursors are first dispensed onto the wafer in liquid form. The coating is subsequently cured to expel the solvent and induce polymerization and crosslinking of the precursors in order to form a solvent-resistant dielectric with desirable electrical, mechanical, chemical, and thermal properties.

Fluorinated oxide shares many integration similarities as undoped plasma oxides and is extensively developed as the next generation ILD with $\kappa = 3.5$ [21]. Fluorinating a

Table 3-2: Families of Candidate Low- κ Dielectrics for Advanced Interconnects

Dielectric Materials	κ	Deposition Method
undoped plasma SiO_2	4.0–4.5	CVD
fluorinated SiO_2	3.5	CVD
spin-on glasses (silsesquioxanes)	2.2–3.0	spin-on
organic polymers (e.g., polyimides, parylenes, aromatic ethers)	2.0–3.9	spin-on / CVD
fluorinated amorphous carbon ($\alpha\text{-C:F}$)	2.1–2.3	CVD
nanoporous dielectrics (e.g., xerogels)	1.2–2.2	spin-on

3.2 Survey of Available Materials

dielectric is a common means of reducing κ provided that the fluorine atoms are incorporated correctly. Fluorine is the most electronegative atom and forms chemical bonds that are not easily perturbed by external electric fields and hence not readily polarizable. However, since fluorine is also highly reactive, excessive fluorination raises concerns of metal and dielectric corrosion. Even though κ as low as 3.2 can be attained, excessive fluorination of oxide additionally introduces moisture uptake and thermal stability issues.

Below κ of 3.5, spin-on glasses (SOG's) have been actively investigated and are already used in production [35]. Before CMP was introduced in manufacturing, SOG's were considered primarily because of their ability to planarize the topography of Al lines and spaces for multilevel integration. Common SOG's are hydrogen silsesquioxane (HSQ) and methyl silsesquioxane (MSQ). Silsesquioxanes or siloxane-based dielectrics are caged silica structures, shown in Figure 3-2, which enclose empty pores for low κ . They are thermodynamically unstable and upon heating at 450°C or beyond, will transform into more densified amorphous SiO_2 , thereby losing its permittivity advantage [72].

Organic polymers have also received significant consideration as ILD materials. Polyimides were first considered because they possess good mechanical strength, thermal stability, and chemical resistance [73] as well as have an established usage in printed cir-

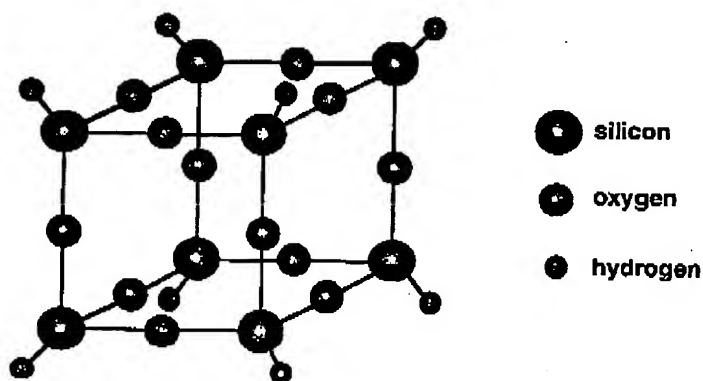


Figure 3-2 Structural formula of a hydrogen silsesquioxane spin-on glass.

Chapter 3: Low-Permittivity Dielectrics

cuit board manufacturing. However, with κ values typically exceeding 3.0, polyimides cannot meet future ILD requirements. Moreover, polyimides readily absorb ambient moisture and exhibit significant anisotropy in the dielectric constant. The polyimide system can be modified to mitigate these limitations, but the improvements are only incremental. These shortcomings have stimulated the chemical industry to develop completely different families of low- κ polymer dielectrics specifically tailored for ILD integration. Some of the spin-on varieties include polyarylene ethers, derivatives of cyclobutane, polynorbornenes, amorphous Teflon™, and phase-separated inorganic-organic hybrids. CVD alternatives include parylene-N, parylene-F, polynaphthalene, and polytetrafluoroethylene (Teflon™). Some of these materials will be further discussed in Section 3.3.

Other dielectrics receiving recent attention include diamond-like carbon [74] and fluorinated amorphous carbon [75]. These materials are attractive primarily because they are deposited by CVD using existing tools. Diamond-like carbon exhibits thermal stability and adhesion issues although it has been successfully incorporated in a single-Damascene demonstration [74]. κ can be reduced to as low as 2.1 by introducing fluorine although fluorination further degrades thermal stability and adhesion.

Nanoporous dielectrics are among the few materials options with ultralow κ (< 2.0). They include xerogels, aerogels, and organic nanofoams [76]. To date, the most active integration effort is with xerogel, a spin-on porous silica matrix. Unlike the previously described families of low- κ dielectrics, κ of xerogel is tunable depending on the degree of porosity that is incorporated during processing. Process integration of porous materials is very challenging because these dielectrics are mechanically weak and have large internal surface areas which can absorb moisture. The pores also degrade dielectric breakdown strength as well as increase the difficulty of depositing continuous films on these dielectric surfaces. Nevertheless, Damascene Cu integration with oxide-encapsulated xerogel has been demonstrated [33]. The potentially significant capacitance advantage of xerogel remains to be shown.

3.3 Investigated Dielectrics

3.3 Investigated Dielectrics

Six low- κ organic polymer dielectrics were studied in this dissertation. As listed in Table 3-3, they consist of five spin-on polymers and one CVD polymer. The chemistries of these materials share some similarities which are incorporated to meet the ILD integration requirements. In designing carbon-based low- κ materials, the most challenging requirement to meet is thermal stability. At temperatures of 400–450°C and beyond, the polymer network begins to disintegrate as there is sufficient thermal energy to break chemical bonds. Thermal stability is improved in polymers which are highly crosslinked and have rigid backbones, aromatic structures, and highly polar groups. Crosslinking additionally increases mechanical strength and solvent resistance. However, aromaticity and polarity increase both κ and water absorption.

Table 3-3: Investigated Low- κ Dielectrics

Low- κ Polymer Family	Specific Variety	κ
polyarylene ether	Schumacher PAE-2 [77]	2.8
	Asahi Chemical ALCAP-E [78]	2.8
aromatic hydrocarbon	Dow Chemical SILK™ polymer [79]	2.7
fluorinated polyimide	DuPont FPI-136M [82]	2.6
benzocyclobutene	Dow Chemical Cyclotene™ 5021 BCB [83]	2.6
arylene-F	Novellus Systems AF-4 [85]	2.4

3.3.1 Polyarylene Ether

Polyarylene ethers consist of aromatic groups (Ar) connected by ether oxygen linkages in a linear fashion. Compared to other functional groups (e.g., carboxylic acids, aldehydes, esters, and ketones), ether linkages provide strong C–O bonds for improved thermal stability while introducing relatively weak polarity for low κ . Two varieties of polyarylene ether were studied: Schumacher PAE-2 [77] (also known as Lo- κ ™ 2000) and Asahi Chemical ALCAP-E [78]. Both materials have very isotropic κ 's of 2.8. See

Chapter 3: Low-Permittivity Dielectrics

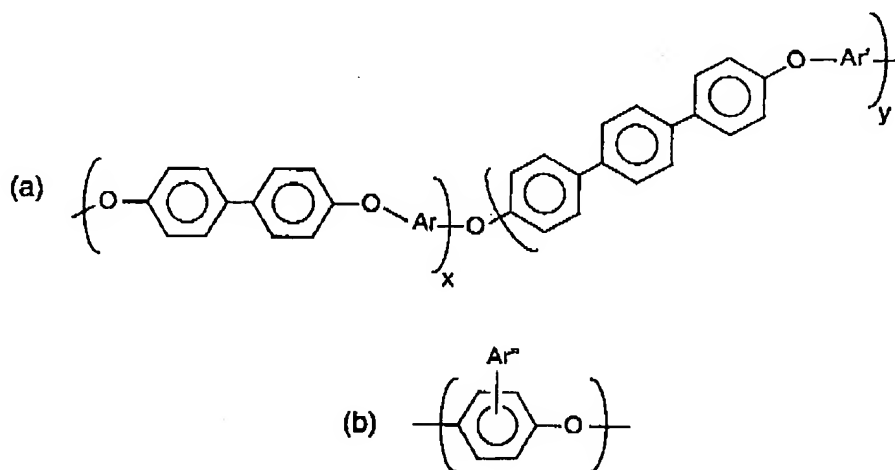
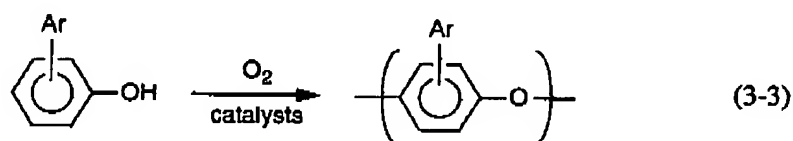


Figure 3-3 Structural formula of two polyarylene ethers: (a) Schumacher PAE-2 [76] and (b) Asahi Chemical ALCAP-E [78]. Ar, Ar', and Ar'' are proprietary aromatic groups.

Figure 3-3. Polyarylene ethers are essentially fully polymerized when spin-coated and can be synthesized by a few approaches. One example is oxidative coupling of phenols, which is employed to synthesize ALCAP-E.



Polyarylene ethers possess many desirable properties for ILD integration but require extensive crosslinking for good thermal stability and solvent resistance. Curing the polymer in oxygen improves crosslinking, but high-temperature exposure to oxygen may not be suitable for Cu integration. Fluorinated polyarylene ether, which exhibit lower κ ($\kappa = 2.5\text{--}2.6$) than nonfluorinated counterparts, has also been synthesized. However, the instability of fluorine in this polymer has resulted in severe metal corrosion, thus rendering integration to be unfeasible.

3.3 Investigated Dielectrics

3.3.2 Aromatic Hydrocarbon

SiLK™ polymer, an aromatic hydrocarbon capable of withstanding temperatures in excess of 500°C, was recently developed by Dow Chemical [79]. Since the chemistry of this polymer is yet to be disclosed, SiLK™ polymer will be generically classified as an aromatic hydrocarbon. This material is an isotropic thermoset resin that becomes highly crosslinked in all dimensions upon curing. Although integration of SiLK™ polymer is very sensitive to processing conditions (e.g., cannot withstand exposure to oxygen at high temperatures) [80], the material is under strong consideration by many companies.

3.3.3 Fluorinated Polyimide

Although conventional polyimides do not meet the κ requirements of future ILD's, fluorinated polyimides are potentially suitable candidates [81], [82]. The specific example that was studied is a copolymer called DuPont FPI-136M (Figure 3-4).

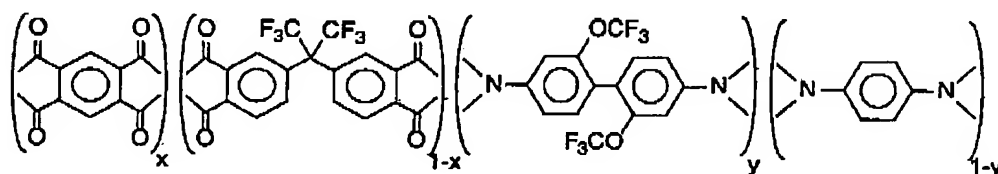
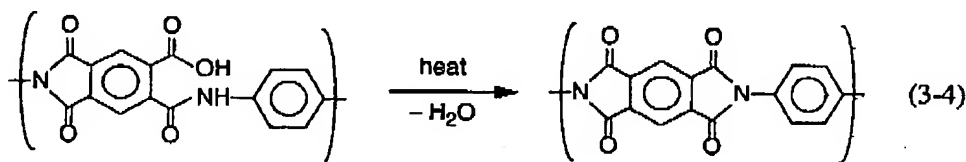


Figure 3-4 Structural formula of DuPont FPI-136M fluorinated polyimide [82].

Fluorinated polyimide exhibits lower κ , lower moisture uptake, and better isotropy than conventional counterparts. Like other linear polyimides, FPI-136M is formed by cyclization of polyamic acid precursors in the curing step after spin-on deposition. A simplified cyclization reaction is illustrated below.



Chapter 3: Low-Permittivity Dielectrics

3.3.4 Benzocyclobutene

Divinylsiloxane-benzocyclobutene (DVS-BCB), commonly known as benzocyclobutene (BCB), is a thermoset resin derivative of cyclobutane deliberately designed to crosslink when heated [83]. The BCB monomer is shown in Figure 3-5.

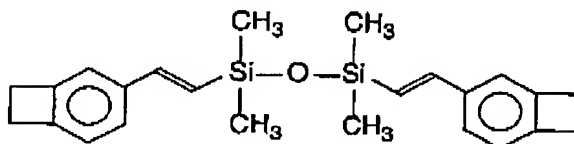
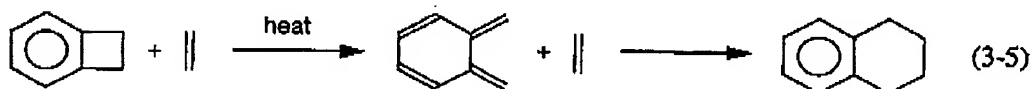


Figure 3-5 Structural formula of Dow Chemical Cyclotene™ 5021 benzocyclobutene (BCB) monomer [83].

Polymerization occurs during the cure step following spin-on deposition. The BCB monomer undergoes a ring opening reaction to give a diene that will react with a C=C to finally give a cyclohexane ring fused to a benzene. Since the BCB monomer has four active sites (two C=C and two cyclobutane rings) for this reaction to occur, the monomer will crosslink into a three-dimensional network, resulting in an isotropic κ of 2.7.



The crosslinking of BCB does not liberate any by-products although the cure must be performed in a non-oxidizing ambient. Otherwise, the polymer will degrade as carbonyl groups (C=O) form. BCB possesses other attractive qualities, such as hydrophobicity, that makes it an attractive and processable low- κ ILD. In fact, Damascene Cu integration with BCB has been demonstrated [84]. Unfortunately, the main drawback of BCB is its limited thermal stability. BCB is stable up to only 350°C and is consequently incompatible with many existing backend processes.

A similar derivative of cyclobutane, also developed by Dow Chemical, is perfluorocyclobutane (PFCB) with $\kappa = 2.4$. However, similar to other dielectrics having fluorine content, the adhesion of PFCB to common backend films is poor.

3.3 Investigated Dielectrics

3.3.5 Parylene-F

Poly(tetrafluoro-*p*-xylylene) or parylene-F is a vapor-deposited crystalline polymer with κ of 2.3–2.4 [85]. See Figure 3-6.

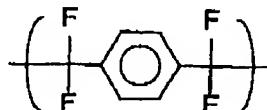
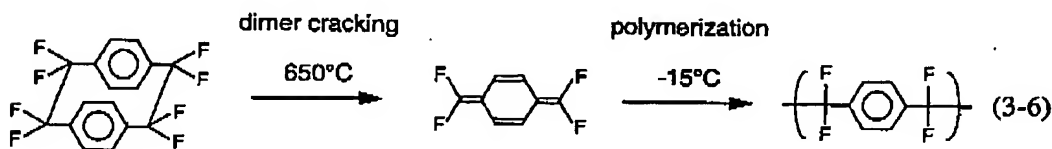


Figure 3-6 Structural formula of Novellus AP-4 parylene-F [85].

Dielectric deposition occurs via a sequence of steps [71]. The process involves first the vaporization (or sublimation) of the di-tetrafluoro-*p*-xylylene dimer at about 150°C. The dimer is led into a reactor where it is cracked, or cleaved, at 650°C to form two reactive tetrafluoro-*p*-xylylene monomers. The monomers are led to a vacuum chamber, condense on the wafer surface which is maintained at -15°C, diffuse into the bulk of the parylene-F film, and then polymerize by reacting with the ends of the free-radical polymer chains. The deposition process is surface-reaction-limited. Therefore, the deposition rate can be dramatically increased by lowering the substrate temperature and increasing the surface absorption rate. After deposition, the film must undergo a vacuum anneal at 350°C to stabilize its properties.



Because parylene-F is deposited from the vapor phase, good conformality can be achieved. Parylene-F has been successfully integrated with conventional Al and W metalization. It is yet to be demonstrated in a Damascene Cu scheme where good gapfill ability is not important. The feasibility of parylene-F for Cu integration is questionable considering the thermal, mechanical, adhesion and dimer cost issues associated with this material.

Chapter 3: Low-Permittivity Dielectrics

3.4 Summary

This chapter reviewed basic properties of low- κ dielectrics and surveyed the families of low- κ dielectrics currently evaluated by the industry. The syntheses and chemistries of the six low- κ dielectrics investigated in this thesis were described. This chapter and the previous chapter presented the prerequisite information for comprehending specific process integration issues of Cu and low- κ polymers—the subjects of the following three chapters. Electrical leakage and anisotropy of fluorinated polyimide are examined in Chapters 4 and 5 respectively while the Cu drift behaviors of the six low- κ polymers of Section 3.3 are evaluated in Chapter 6.